

MICROWAVE HEATING FOR PRODUCTION OF A GLASS BONDED CERAMIC HIGH-LEVEL WASTE FORM

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ABSTRACT

Argonne National Laboratory has developed a ceramic waste form to immobilize the salt waste from electrometallurgical treatment of spent nuclear fuel. The process is being scaled up to produce bodies of 100 Kg or greater. With conventional heating, heat transfer through the starting powder mixture necessitates long process times. Coupling of 2.45 GHz radiation to the starting powders has been demonstrated. The radiation couples most strongly to the salt occluded zeolite powder. The results of these experiments suggest that this ceramic waste form could be produced using microwave heating alone, or by using microwave heating to augment conventional heating.

INTRODUCTION

During much of the ceramic waste form development effort, a hot isostatic press (HIP) was used to consolidate the powder starting materials. The HIP applies heat and pressure to melt the glass binder and consolidate the powder into a dense solid body. This fabrication route was necessary when the desired end product was a glass-bonded zeolite. Processing temperatures had to be kept relatively low to avoid transforming the zeolite to sodalite, with concurrent release of excess salt. The low processing temperature required the use of pressure to achieve densification. With the selection of glass-bonded sodalite as the final waste form (which necessitated a reduction in salt loading), higher processing temperatures could be used for consolidation. At the higher processing temperatures used to fabricate the glass-bonded sodalite waste form, densification could be achieved without the application of pressure. The current baseline process for fabricating the glass-bonded sodalite waste form achieves densification using heat only, and is called "pressureless consolidation."

As the size of the waste form is scaled up from laboratory scale (on the order of a few centimeters in diameter) to full scale (about 1/2 meter in diameter),

heating material in the center of the powder charge becomes more difficult. Thermal conductivity through the loose powder is relatively low, so as the size of the waste form increases, processing time must also be increased to fully densify the material. In the HIP process, this problem was partially alleviated by the application of pressure, since pressure drives densification, and thermal conductivity increases with density. However, since the baseline process for fabricating the glass-bonded sodalite waste form relies solely on temperature to achieve densification, processing times for the full-scale waste form may become excessive.

Commercially available microwave ovens operating at 2.45 GHz and at power levels from 450 to 850 W have been used to heat zeolites and other aluminosilicates.^{1,2} One advantage of microwave heating is that heat is evolved within the load as microwave energy penetrating the material is absorbed. This results in rapid heating of the load. At 600 W, complete melting of a 10 g, 2.5 cm diameter pellet of Linde 4A was achieved in less than 2 min.¹ It has been proposed that the initial heating of zeolite 4A (below about 400° C) depends on the degree of hydration, and that dehydrated zeolite could be difficult to heat with microwave radiation alone.³ The zeolite material used to fabricate the glass-bonded sodalite waste form contains essentially no water (< 0.5 wt. %), but does contain approximately 2.5 molecules of occluded chloride salt per pseudo unit cell. The starting material for the glass-bonded sodalite waste form also contains 25 wt. % borosilicate glass. The microwave heating behavior of these materials, alone or in combination, has never been reported in the open literature.

The objectives of this work were therefore to determine whether microwave energy would couple sufficiently with the starting material for the glass-bonded sodalite waste form to cause heating, and, if so, to determine if microwave heating could be applied to a production process.

EXPERIMENTAL

In order to heat materials to high temperatures in a conventional microwave oven, thermal energy generated within the load must not be allowed to escape freely into the microwave cavity. For these experiments, an insulating chamber with internal dimensions 5 cm by 5 cm by 7.5 cm high was constructed from 2.5 cm thick Zircar[®] ECO-1200B refractory insulating board. When inserted, the 50 ml high purity alumina crucibles used for these experiments nearly fill this chamber.

Experiments were performed in two phases. In phase 1, the objective was simply to determine if glass-bonded sodalite starting materials would couple to a microwave field efficiently enough to achieve high temperatures. An uninstrumented commercial microwave oven (CEM model MDS81D) with a nominal power output of 850 W at 2.45 GHz was used to qualitatively evaluate

the coupling efficiency of the glass-bonded sodalite waste form starting materials separately and as the standard starting mixture. In these experiments, incandescent light escaping through joints in the insulating chamber served as an indicator that the load had reached high temperature. The elapsed time from application of microwave power to observation of incandescent light was used as a relative measure of coupling efficiency.

The objective of phase 2 experiments was to quantify the thermal response of the glass-bonded sodalite waste form starting material to a microwave field to allow assessment of potential production applications. For these experiments, a commercial Magic Chef model MCD990B with a nominal power output of 900 W at 2.45 GHz was modified to accept a metal sheathed, ungrounded type K thermocouple. A small hole was drilled through the roof of the oven to allow insertion of the thermocouple, and a corresponding hole was drilled through the roof of the insulating chamber so that the thermocouple could be inserted into the center of the load.

The materials used in these experiments were a dehydrated, salt occluded zeolite 4A from UOP (Des Plaines IL), and a borosilicate glass frit from Pemco Corp. (Baltimore MD). Both materials were in powder form, with a nominal particle size of -60+200 mesh. The composition of the glass is given in Table I.

Table I: Composition (as oxides) of the glass frit used to make the glass-bonded sodalite waste form

Compound	Weight Percent
SiO ₂	66.5
B ₂ O ₃	19.1
Al ₂ O ₃	6.8
Na ₂ O	7.1
K ₂ O	0.5

Salt occluded zeolite 4A was prepared by first drying zeolite 4A at 550° C under vacuum, then loading the dried zeolite with simulated (non-radioactive) electrorefiner salt (8.33/1 zeolite to salt mass ratio) at 500° C in a heated V-mixer. The composition of the salt is shown in Table II.

Table II: Composition of the salt used to make the salt occluded zeolite used in these experiments

Salt	Wt. %	Salt	Wt. %
LiCl-KCl eutectic	69.7	BaCl ₂	1.02
NaCl	14.9	LaCl ₃	1.22
KBr	2.3 X 10 ⁻²	CeCl ₃	2.33

RbCl	0.33	PrCl ₃	1.15
SrCl ₂	1.01	NdCl ₃	3.89
YCl ₃	0.70	PmCl ₃	0.11
KI	0.15	SmCl ₃	0.69
CsCl	2.50	EuCl ₃	4.71 X 10 ⁻²

RESULTS AND DISCUSSION

Phase 1 Experiments

In the first phase 1 experiment, 14.8 g of salt occluded zeolite 4A was loaded into the crucible, filling it about half way. Power was switched on, and incandescence was observed after 225 s. Power was immediately switched off. After cooling, the crucible was removed and examined. Most of the powder appeared unaffected, but a region in the center was cracked and seemed to have begun to sinter. There was a hollow space below this region, at the bottom of which was about a 1 cm piece of material that had melted.

The first experiment was repeated with 14.6 g of glass frit as the load. After three consecutive 10 min runs, the oven was opened and the lid of the insulated enclosure removed to observe the load. The glass powder was quite warm, so another pre-programmed run, this time for 30 min was initiated. Incandescence was observed 503 s into that run. After the crucible had cooled, visual observation showed that approximately half the glass had melted.

The same experiment was repeated with 14.8 g of a 3/1 mixture (by weight) of salt occluded zeolite 4A to glass frit. Incandescence was observed 239 s into the run. After cooling, visual examination revealed that a small portion of the charge had consolidated into a spheroid about 1.5 cm in diameter by 1 cm thick. The results of these experiments are summarized in Table III.

The results of the phase 1 experiments show that both the salt occluded zeolite 4A and the borosilicate glass frit used to make the glass-bonded sodalite waste form can be heated to high temperatures in a microwave field. However, the

Table III. Results of phase 1 microwave heating experiments at a nominal microwave power of 850 W

Material	Mass of load (g)	Time to Incandescence (s)
Salt Occluded Zeolite 4A	14.8	225
Borosilicate Glass Frit	14.6	>1800
3/1 (weight) mixture of Salt Occluded Zeolite to Glass	14.8	239

salt occluded zeolite clearly couples more efficiently to the microwave field than the glass. As can be seen from Table III, the thermal response of the 3/1 (by

weight) mixture of salt occluded zeolite to glass used to make the glass-bonded sodalite waste form closely resembles the thermal response of the pure zeolite. This implies that at least initially the salt occluded zeolite component is performing the energy conversion function that heats the entire mixture.

The rapid onset of incandescence in both materials is typical of the phenomenon known as thermal runaway, that has been widely reported in the literature.^{2,3,4} This phenomenon can seriously limit the use of microwave heating for production applications. This is especially true for the glass-bonded sodalite waste form, because melting causes the radionuclide-bearing salt to phase separate into halide inclusions that are readily soluble in water. So, while the phase 1 experiments showed that glass-bonded sodalite waste form starting materials can be heated to high temperatures using microwave radiation, the question of whether microwave heating could be used in waste form production remained unanswered.

Phase 2 Experiments

Some way to control or avoid thermal runaway is necessary to use microwave heating in the glass-bonded sodalite waste form production process. The phase 2 experiments addressed this problem by first quantifying the thermal response of the starting mixture to identify the onset of thermal runaway, then testing the microwave duty cycle (power setting) as a means of controlling the temperature of the load.

A type K thermocouple was inserted approximately into the center of 22.68 g of the salt occluded zeolite 4A/glass baseline mixture for making the glass-bonded sodalite waste form. The first experiment was run logging temperatures every 10 s. After 70 s, the temperature jumped from about 400° C to nearly 1200° C, indicating the onset of thermal runaway (see Figure 1). Power was immediately shut off, and the load allowed to cool. While cooling, several power settings above and below 7 were tested. Below 7, the load continued to cool, and above 7 temperature increased to thermal runaway.

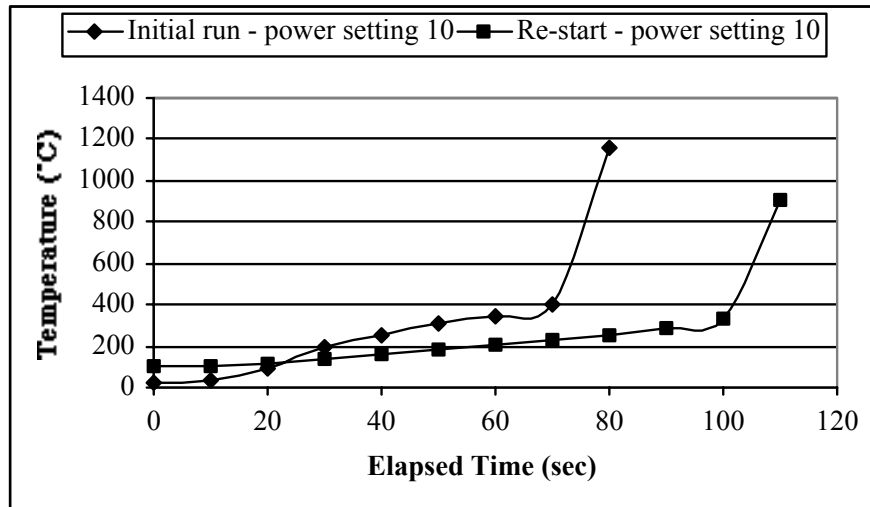


Figure 1: Plot of temperature vs. time for the two full power thermal runaway events encountered during the phase 2 experiments.

The load was allowed to cool to about 100° C, whereupon heating at full power was re-initiated. Thermal runaway was again encountered, although at a slightly longer elapsed time (see Figure 1). Power was switched off, and when the load cooled to about 600° C, heating was re-initiated at a power setting of 7 (70% duty cycle, about 20 s on and 10 s off). At this setting, the temperature quickly rose to about 950° C, then began to oscillate with the duty cycle. Monitoring the temperature for about three minutes indicated that the load was approaching dynamic equilibrium, with a mean temperature around 900° C (see Figure 2). This heating schedule was continued for ten minutes, whereupon the programmed run was automatically terminated. Heating was immediately re-initiated at a power setting of 7 for a programmed time of 30 min, but the oven shut down automatically in response to an overtemperature protection device after 657 s. The experiment was terminated at that point.

After cooling, a spheroid approximately 1 cm in diameter was found loosely attached to the thermocouple. The remainder of the powder was apparently unaffected. The solid piece was easily dislodged from the thermocouple, and sectioned for analysis. It appeared to consist of two distinct layers; a friable, poorly consolidated layer on the outside, and a well consolidated core on the inside. Optical and scanning electron microscopy revealed that the inner core consisted of a multi-phase outer layer and an amorphous-looking inner core (see Figure 3).

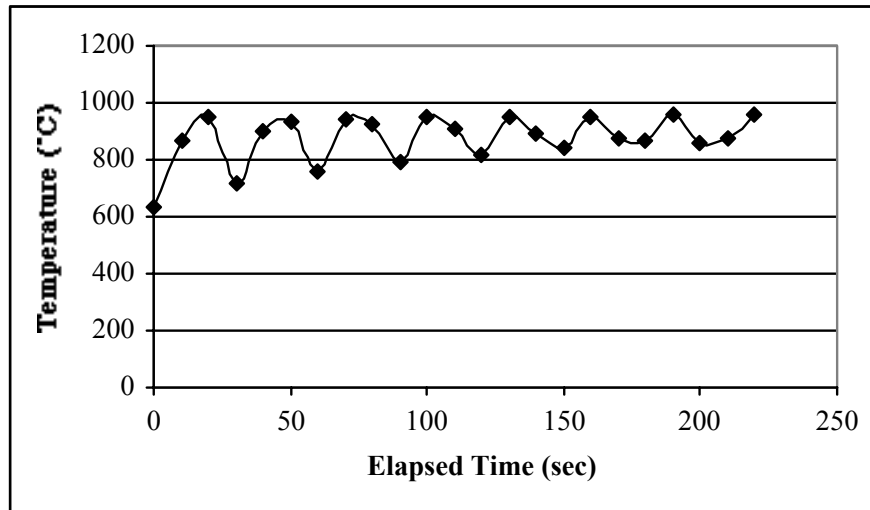


Figure 2: Plot of temperature vs. Time at 70% duty cycle showing approach to dynamic equilibrium at a temperature of about 900° C.

Figure 3: Optical micrograph showing the multiple layers of the solid body formed in the phase 2 heating experiments. Tick marks on the scale at the bottom are one millimeter apart.

Except for excess porosity near the inner glassy core, the outer portion of the well-consolidated material resembles normal glass-bonded sodalite waste form material. X-ray powder diffraction confirmed the phase composition as resembling the conventionally prepared waste form, except with a bit more

nepheline (in this case a thermal decomposition by-product of sodalite). The outer, poorly consolidated layer showed less halite (a by-product of glass/sodalite interactions) and a lower amorphous content than the inner portion. These results are consistent with the visual observations evident in figure 3.

CONCLUSIONS

Glass-bonded sodalite waste form starting materials, particularly the salt occluded zeolite, effectively couple to microwave radiation resulting in heating. While thermal runaway resulting in undesirable melting is possible, simple duty cycle power modulation appears to give sufficient temperature control to make microwave heating for waste form production feasible. Further testing is required to determine how best to apply microwave heating. For example, microwave heating could be used exclusively for producing glass-bonded sodalite waste forms, or it could be used as a boost in conjunction with conventional heating to accelerate heating of the central portion of full-scale waste forms, thereby reducing processing times. Future experiments are planned to address this question.

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